Vapor-Liquid Equilibria in the System 2-Propanol–2,2,4-Trimethylpentane

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As part of a program to study the behavior of alcohol-hydrocarbon systems, the vapor-liquid equilibrium data for the system 2-propanol–2,2,4-trimethylpentane have been determined under isobaric conditions at 760 mm. of mercury. A vapor-recirculation equilibrium still was used. Refractive index measurements were used for analysis. The experimental results are found to be thermodynamically consistent by means of the method of Redlich and Kister. The azeotrope was found to contain 64 mole % of 2-propanol, boiling at 77.3° C.

The only reference obtainable to vapor-liquid equilibrium in the 2-propanol–2,2,4-trimethylpentane system is that reported by Lecat (*8*): azeotrope, at 760 mm. of mercury, contains 54% (69 mole %) of 2-propanol, boiling at 76.8° C. [see also Horsley (*5*)].

APPARATUS

The equilibrium determinations were carried out in an all-glass, electrically heated, vapor-recirculation still. This type of still, originally devised by Jones, Schoenborn, and Colburn (*7*), was used in the slightly modified form as described by Griswold and Buford (*4*).

Equilibrium temperatures were measured by means of a mercury in glass thermometer which had been previously compared with a thermometer certified by the National Bureau of Standards. A ₮ 10/30 ground joint was connected to the upper part of the equilibrium chamber, and the thermometer, provided with the corresponding inner joint, was introduced here. Another ground joint with the corresponding stopper was attached to the upper part of the condensate chamber. This arrangement made unnecessary the stopcocks which are connected to the bottom of the equilibrium chamber and the condensate chamber in the original design. Both liquid and vapor-condensate samples were taken by means of a hypodermic syringe provided with a special long needle, and transferred immediately into receptacles cooled in ice water. The equilibrium still was connected to a manostat which allowed the pressure to be maintained constant at 760 mm. of mercury, within ±1 mm. A pressure-regulating system similar to that described by Baker, Hubbard, Huguet, and Michalowski (*1*) was used. After smooth operation of the still was obtained, 50 minutes were allowed to establish equilibrium. Samples of liquid and vapor-condensate were then withdrawn and analyzed.

In order to verify the proper functioning of the still, some determinations were carried out with ethanol-water mixtures. The data obtained were in good agreement with those reported in the literature.

MATERIALS AND ANALYSIS

C. P. grade 2-propanol was dried over freshly calcined calcium oxide and fractionated in a column as described by Todd, (*14*), provided with a Podbielniak packing (*9*). The entire batch distilled at 82.2° C. (760 mm. of mercury), and the arbitrarily subdivided fractions all had the same refractive index.

2,2,4-Trimethylpentane of technical grade was obtained from the Eastman Kodak Co. It was filtered through a tube packed with silica gel to remove olefins, and distilled in an efficient column, packed with Raschig rings. Heart cuts of constant refractive index were used for the experimental work. The constants of the purified materials are,

	2-Propanol			2,2,4-Trimethylpentane		
	Exptl.	Lit.		Exptl.	Lit.	
n_D^{25}	1.37505	1.3749	(*3*)	1.38908	1.38898	(*3*)
d_4^{30}	0.7761	0.77690	(*13*)	0.68341	0.68366	(*3*)
Normal b. p., ° C.	82.2	82.18	(*3*)	99.2	99.23	(*3*)

Refractive indices were determined with a Bausch & Lomb precision refractometer (sugar) using a sodium vapor lamp illuminator. The temperature of the prisms was maintained constant within ±0.05° C. by a Precision Scientific constant-temperature circulator.

Twelve mixtures of the purified liquids were prepared gravimetrically. To avoid evaporation, a short rubber tube, one end closed by a plug of glass, was connected to the mouth of a 60-ml. bottle. A hypodermic needle was introduced into the rubber tube, and the bottle was evacuated by means of a vacuum pump. The empty bottle was weighed. The first component of the mixture was injected by means of a hypodermic syringe. After the bottle had been reweighed, the second component was introduced in the same manner, and the final weight determined.

Three samples of each mixture were taken and placed directly between the prisms of the precision refractometer, which were kept at 30° C.

A large graph of n_D^{30} against mole fraction of 2-propanol was prepared and used to determine the compositions of the equilibrium mixtures.

EXPERIMENTAL RESULTS

The boiling points under isobaric conditions (760 mm. of mercury) and the equilibrium concentrations are given in the first three columns of Table I. Figure 1 shows the relationship between vapor and liquid composition at equilibrium at 760 mm. of mercury. According to these data the azeotrope contains 64 mole % of 2-propanol.

CORRELATION OF RESULTS

The results were examined for thermodynamic consistency by application of the integrated approximation forms of the Gibbs-

Table I. Vapor-Liquid Equilibrium Data and Activity Coefficients for 2-Propanol–2,2,4-Trimethylpentane at 760 Mm. of Mercury

Temp., °C.	Mole Fraction 2-Propanol		Activity Coefficients	
	Liquid, x_1	Vapor, y_1	γ_1	γ_2
99.2	0.000	0.000	. . .	1.000
93.5	0.029	0.177	3.951	1.000
89.4	0.058	0.293	3.810	1.000
83.6	0.121	0.435	3.396	1.023
80.2	0.230	0.526	2.480	1.091
79.1	0.331	0.555	1.903	1.222
78.6	0.390_5	0.573	1.701	1.308
77.8	0.517	0.602	1.395	1.579
77.6	0.613	0.630	1.242	1.843
77.3	0.676_5	0.654_5	1.184	2.080
78.1	0.800	0.720	1.065	2.656
78.4	0.878	0.780	1.038	3.388
80.2	0.957_5	0.895	1.014	4.381
82.2	1.000	1.000	1.000	. . .

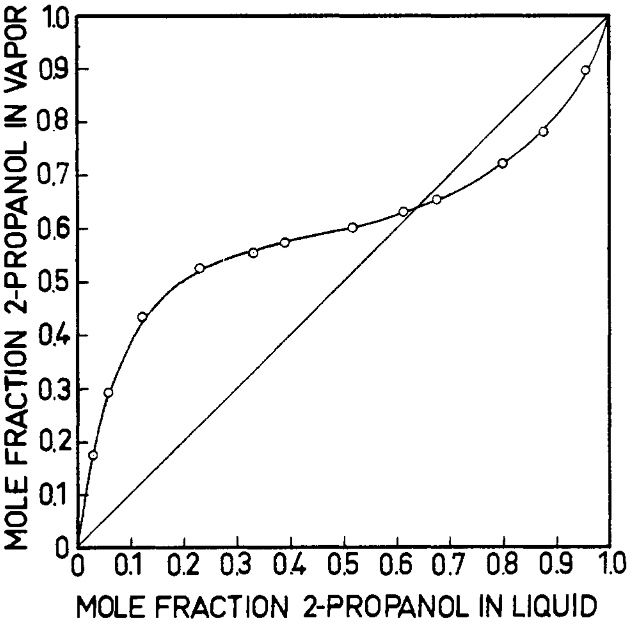

Figure 1. Relationship between vapor and liquid compositions at equilibrium for 2-propanol–2,2,4-trimethylpentane at 760 mm. of mercury

Duhem equation, as developed by van Laar and by Redlich and Kister. For this purpose, the activity coefficients of the two components, given in columns 4 and 5 of Table I, have been calculated using the equations

$$\text{(2-Propanol) } \gamma_1 = \frac{y_1 760}{x_1 p_1^0}; \text{ (2,2,4-trimethylpentane) } \gamma_2 = \frac{y_2 760}{x_2 p_2^0}$$

where x and y are, respectively, liquid and vapor compositions (mole fractions). p_1^0 and p_2^0 (mm. of mercury), the vapor pressures of the pure components at the equilibrium temperatures, were calculated from the following Antoine equations, using the values of the constants given by Dreisbach (*3*).

$$\text{(2-Propanol) } \log p_1^0 \text{ (mm. Hg)} = 6.66040 - \frac{813.055}{132.93 + t\ ^\circ\text{C.}}$$

$$\text{(2,2,4-Trimethylpentane) } \log p_2^0 \text{ (mm. Hg)} = 6.81984 - \frac{1262.490}{221.271 + t\ ^\circ\text{C.}}$$

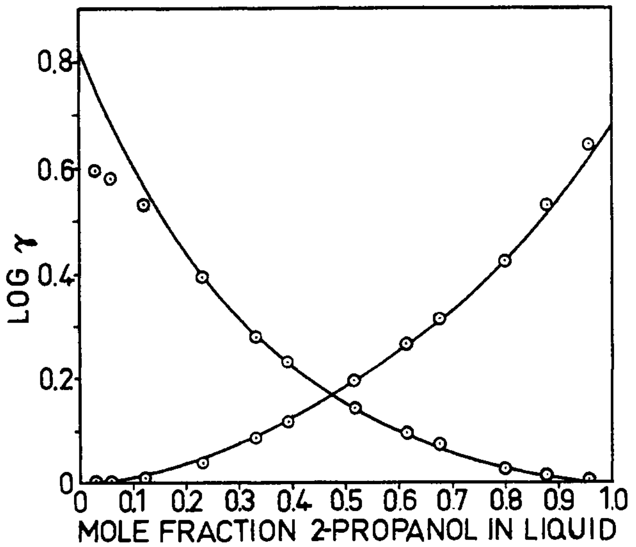

Figure 2. Logarithms of activity coefficients at 760 mm. of mercury

o Experimental values
— Calculated from Equations 3 and 4

These equations fit the data obtained for the boiling points of the pure liquids, determined at 760 mm. of mercury in the equilibrium-apparatus, within the limits of experimental error.

No corrections were applied to account for the nonideality of the vapor phase in the evaluation of the activity coefficients.

It was found that the van Laar equations in the symmetrical form, as given by Carlson and Colburn (*2*), could be used to represent the activity coefficients fairly well using the constants $A = 0.757$ and $B = 0.591$.

A better agreement with the experimental data is obtained by the following series which, based on the function Q, were developed for the activity coefficients by Redlich, Kister, and Turnquist (*12*).

$$\log \gamma_1 = x_2^2\,[B + C(3x_1 - x_2) + D(x_1 - x_2)(5x_1 - x_2) + \ldots] \quad (1)$$

$$\log \gamma_2 = x_1^2\,[B + C(x_1 - 3x_2) + D(x_1 - x_2)(x_1 - 5x_2) + \ldots] \quad (2)$$

As expected in the case of a solution which contains an associated component, three constants (B, C, and D) proved to be necessary to represent the activity coefficients of the system. With the values $B = 0.6824$, $C = 0.068$ and $D = 0.0644$, the equations for the activity coefficients are:

$$\log \gamma_1 = x_2^2\,[0.798 - 0.758x_2 + 0.773x_2^2] \quad (3)$$

$$\log \gamma_2 = x_1^2\,[1.208 - 1.302x_1 + 0.773x_1^2] \quad (4)$$

According to Redlich and Kister (*11*) the high value of constant D, the so-called association term, is to be expected for a strongly associated system.

In Figure 2 ($\log \gamma$ *vs.* x_1) the values calculated from experimental data are represented by circles, and the solid lines are calculated from Equations 3 and 4 which satisfy the "area condition" derived by Redlich and Kister (*10*).

The deviations at the extremes of the concentration range, especially those of the first three points of $\log \gamma_1$, from the calculated curve are almost certainly due to the higher temperature (83.6 to 93.5° C. compared with 77.3 to 80.2° C. for the other points)—i.e., to the fact that Equations 1 and 2 are strictly valid only at constant temperature. For the system 2-propanol–2,2,4-trimethylpentane, the boiling interval is not very large, so that Equations 1 and 2 could be expected to hold fairly well. However, as shown by Ibl and Dodge (*6*), even for close-boiling mixtures the degree of inaccuracy in the extremes of the concentration range may be rather large. This does not exclude the possibility that the deviations might be due, at least in part, to the nonideality of the vapor phase or even to experimental errors.

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